

# PATENT SPECIFICATION

(11) 1 369 047

1 369 047

- (21) Application No. 45620/71 (22) Filed 30 Sept. 1971  
 (31) Convention Application No. 85119 (32) Filed 30 Sept. 1970  
 (31) Convention Application No. 90297 (32) Filed 13 Oct. 1970 in  
 (33) Japan (JA)  
 (44) Complete Specification published 2 Oct. 1974  
 (51) International Classification B29J 1/00; B01J 11/52  
 (52) Index at acceptance  
 B5A 1R100 1R58 1R64 1R66  
 B1E 277 308 330 33Y 341 342 34Y 375 37Y 382 38Y 400  
 40Y 420 42Y 44Y 551 55Y 570 571 580 645 651  
 677 691 69X



## (54) MOULDING METHOD AND PACKING STRUCTURE FOR CATALYST FOR USE IN PURIFICATION OF WASTE GAS CONTAINING CARBON MONOXIDE

(71) We, MITSUI MINING & SMELTING CO. LTD., a Japanese Company, of No. 1—1, 2-chome, Nihonbashi-Muromachi, Chuo-Ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method of moulding a catalyst for use in the purification of waste gases containing carbon monoxide, comprising admixing a mixture consisting mainly of manganese oxides and a lead or bismuth oxide—preferably said mixture plus some metals or metal oxides—with some metallic powder having a satisfactory compactibility added thereto as occasion demands; subjecting the resulting mixture to compacting at a temperature from 200—700° C., preferably 300—500° C., and it also relates to the packing structure composed of the thus moulded catalysts assembled or piled up so as to be capable of functioning most efficiently in purifying a waste gas containing carbon monoxide.

Waste gases exhausted from gasoline engines used in automobiles contain undesirable components such as hydrocarbons and nitric oxides, as well as carbon monoxide in large quantities. Waste gases containing carbon monoxide are also generated by internal combustion engine used to power aircraft, construction machinery and so on, factories, and is therefore widespread. As means of converting carbon monoxide, which accounts for the greater part of the harmful gases generated, into harmless carbon dioxide gas by oxidation, there has hitherto been proposed the use of a catalyst consisting mainly of manganese oxides and lead oxides or a catalyst consisting mainly of manganese oxides and bismuth oxides. Such catalysts for use in purification of waste gases containing carbon monoxide having either of

the foregoing compositions (hereinafter referred to as the metal-oxide catalyst) have proved capable of efficiently oxidising carbon monoxide and are therefore extremely effective in purifying waste gases. However, most of these catalysts in the prior art are in the form of pellets or else the catalyst is supported on a porous substance. And, as manufacturing processes therefor, the following methods are popular: a method of producing a globular or pellet-shape product from a mixture composed of metal oxides constituting the catalytic component and an appropriate amount of various binders added thereto by known process steps such as subjecting the mixture to granulating, or pelletising while it is wet, and drying and sintering; a method of producing an oxide catalyst, through the process of applying water-soluble salts of a catalytic component onto the surface of a refractory porous substratum having honeycomb structure or the like and calcining it thereafter. According to the former method, however, the pellets of metaloxide catalyst get pulverised as a result of mutual collision or friction due to the vibration arising from the cruising of the automobile, whereby the passage for waste gas becomes clogged, leading to not only the lowering of the efficiency of the engine but also the deterioration of the functioning of the catalyst which involves also the risk of discharging the harmful heavy metal oxides contained therein from the catalyst container to the outside. According to the latter method on the other hand, inasmuch as the refractory porous substratum consisting of an inert substance having no catalytic function accounts for more than 50% of the total weight of the product, the resulting catalyst is defective in that its life span is short. In addition to the above, as a method of compacting of metal oxide catalysts, there is known a method comprising the steps of mixing the material powder with various binders

and/or lubricants, subjecting the thus prepared material to compacting and subsequent sintering at a temperature above 1000° C. for a long period of time or some other heat treatment similar thereto, but this method is not advisable in view of the fact that it requires heat treatment at a high temperature for hours and complicated process steps involving expensive equipment. Besides, in the case of metal oxide catalysts, as the metal oxide powder is apt to change its quality when it undergoes sintering at a high temperature so that its catalytic function deteriorates, it is unadvisable to adopt the conventional methods mentioned above in compacting the metal oxide catalyst.

In the meantime, there have hitherto been proposed various forms of apparatus for the purification of the waste gases generated by the automobile. But, the catalyst containers for use in the conventional apparatuses mostly contain a large quantity of irregularly-packed fine catalyst pellets (hereinafter called pellet-packed structure) and have various defects, so that some other packing structure suitable for said purpose has been sought. The important defects of the conventional structure are summarised as follows:

- (i) The catalyst pellets are apt to become unevenly packed due to vibration during the operation of the automobile.
- (ii) Mutual friction between the pellets causes abrasion and pulverisation thereof, thereby encouraging uneven packing of the pellets.
- (iii) As a result of the packing becoming uneven, the currents of waste gases are unevenly distributed, thereby increasing the resistance to gas flow and causing deterioration of the purification efficiency.
- (iv) As the inter-pellet thermal conductivity is poor and the thermal radiation is not effected smoothly, the temperature distribution becomes uneven and the life span of the catalyst is shortened.
- (v) There is the risk of powdered catalyst being expelled along with the waste gas.

As the catalyst capable of effectively working for a long period in oxidation and purification of the waste gas arising from the gasoline engine in use for automobiles, etc., there have hitherto been proposed a catalyst mainly composed of manganese oxides and lead oxides and a catalyst mainly composed of manganese oxides and bismuth oxides (so-called metal-oxide catalysts). Either of these catalysts may also include a quantity of at least one member selected from oxides of alkaline earth elements such as Mg, Ca or Ba, oxides of rare earth elements such as Y, La, Ce or Nd, oxides of Al, Si and Bi, oxides of such transition metal as Cu, Fe, Co, Ni, etc., or transition metals such as Cu, Fe, Co or Ni; or Sn or Al. Throughout this specification, the term "rare earth element" includes lanthanum and yttrium as

well as the lanthanides. These metal-oxide catalysts containing such additives are more effective in purifying the waste gas by means of mainly oxidising carbon monoxide contained therein. It has now been found that a compacted catalyst (catalyst element) having superior mechanical strength can be produced by subjecting any of the above-mentioned metal-oxide catalyst powders (with or without any of the above-mentioned additives) to hot pressing at such temperatures as will not cause any deterioration of the components thereof.

According to the invention, we provide a method of moulding a catalyst element for use in purification of waste gas containing carbon monoxide, comprising compacting a catalyst powder composed mainly of a manganese oxide and either lead oxide or bismuth oxide to compacting at a temperature from 200—700° C., and at a pressure of 1—10 tonne/cm<sup>2</sup>. The temperature is preferably from 300—500° C. and the pressure is preferably from 2—5 tonne/cm<sup>2</sup>. The invention also relates to a catalyst-packing structure, i.e. a sort of block-assembly structure consisting of said catalyst elements regularly assembled or piled up in a specified disposition so as to make them function most effectively.

If the temperature is too low, the strength of the moulded catalyst is insufficient, while if the temperature is too high, there is the risk of changing the quality of manganese oxides. If the pressure applied is below the minimum of the above-mentioned range, the resulting moulded catalyst is of insufficient strength, while if the pressure exceeds the maximum of said range, there is the risk of damaging the die for use in compacting.

The applicable mixing ratio of manganese oxides to lead oxides in the metal-oxide catalyst is in the range of about 75:25 to about 25:75—preferably about 60:40 to about 40:60 by wt. The applicable mixing ratio of manganese oxides to bismuth oxides is in the range of about 95:5 to about 50:50—preferably about 90:10 to about 70:30 by wt. As to the applicable mixing ratio of the additives to be mixed with the principal components, where the additives is at least one member selected from the above mentioned additives, the mixing ratio thereof against the principal components is in the range of about 5 to 10 wt%—preferably about 7—8 wt% except where the additive is a bismuth oxide and the principal components are manganese oxide and lead oxide, the mixing ratio of the bismuth oxide is in the range of about 5 to 40 wt%—preferably about 5—30 wt%—of the whole amount of the principal components. Where the additive is a transition metal and the principal components are manganese oxide and lead oxide, the mixing ratio of the additive is in the range of about

5 to 40 wt%—preferably about 5 to 30 wt%—of the whole amount of said principal components, while where the principal components are manganese oxide and bismuth oxide, said mixing ratio is in the range of about 5 to 60 wt%—preferably about 10—30 wt%—of the whole amount of said principal components.

The thus prepared metal-oxide catalyst element in the present invention is very suitable for use in the purification of the waste gas from automobiles. The amount of this catalyst element to be employed in an automobile depends on the volume of exhaust produced and the shape of the catalyst element can be so formed as to augment the area coming into contact with the waste gas and at the same time to be convenient for fitting into its container. For the purpose of augmenting the area coming into contact with the waste gas, it is desirable for the surface of the catalyst element to be wrinkled or corrugated and/or have penetrating holes.

The catalyst element prepared as above is packed so as to form a block-assembly structure. Accordingly, the catalyst element capable of rendering the most effective packing structure for use in purification of the waste gas is a compacted catalyst capable of filling the cross-sectional area of the catalyst container most efficiently, for instance, such one as presenting a regular section composed of straight lines or curves, e.g. a polygon, circle, or sector, and the optimum packing structure for purification of waste gas can be provided by means of a prescribed regular disposition of thus prepared catalyst element having a fixed configuration. An example of a packing structure applicable in assembling the catalyst element within a catalyst container is as follows: the circumference of a circle circumscribing the first catalyst element is to be the same as the inner circumference of the catalyst container, and the second catalyst element, third catalyst element and so on are to be identical to the first catalyst element and be piled onto the first catalyst element in order. Further, it is advisable to provide the surface of the compacted catalyst with corrugations or wrinkles so as to secure effective voids and areas to contact with the waste gas as a result of packing of the catalyst elements. Also, it may be convenient to form a perforated portion having a prescribed sectional area inside the element. To cite more concrete examples of the packing structure, if the catalyst container is of cylindrical shape, the first catalyst element may be annular with a corrugated or wrinkled surface coming into close contact with the catalyst container, the second catalyst element, the third catalyst element and so on, which are similar to the first catalyst element in shape being fitted concentrically and successively into the hole in the annular first element, whilst if the catalyst container is rectangular, it is convenient to

apply such a structure as consisting of the first catalyst element shaped into a flat plate having a corrugated or wrinkled surface, the second catalyst element, the third catalyst element and so on, which are all practically similar to the first catalyst element in configuration and size and are piled up thereon one after another.

Some merits of the present invention are as follows: i) it is possible to change the configuration of the catalyst element, so that augmentation of the contact area is feasible; ii) inasmuch as the catalyst elements are built up into a block-assembly structure and the surface of the catalyst is brought into close contact with the catalyst container, the packed catalyst does not become displaced even by vibration during the running of automobiles, and the passage of the waste gas shows little change as hardly any pulverisation of the catalyst elements occurs in the absence of mutual collision or friction between them, and, as a result, not only can a stable catalytic function be expected, but also there is little risk of any pulverised catalyst being lost to the outside; iii) by means of an appropriate selection of the configuration of catalyst element as well as the assortment thereof, it is possible to facilitate the passing of waste gas thereby preventing the lowering of the efficiency of the engine, to augment the area for mutual contact between the waste gas and the catalyst element, and to secure a constant function of the catalyst; iv) the catalyst element has a fixed cross-sectional configuration as well as thickness, so that it is not only suitable for mass production but also convenient for assembling or handling, and is therefore very economical; v) it is possible to build a packing structure having sound-muffling effect, so that the packing structure of the present invention can be concurrently utilised as a muffler.

Some embodiments of the invention are exemplified in the accompanying drawings. The arrows in Figures 5 to 8 show the direction of gas flow.

Figure 1 is a plan view of one configuration of the catalyst element according to the present invention.

Figure 2 is a cross-sectional view taken along the line (II)—(II') in Figure 1.

Figure 3 an end view of a structure of an assembly consisting of a plurality of catalyst elements shown in Figure 1, said assembly formed for readiness of being packed in a catalyst container.

Figure 4 a schematic cross section of the catalyst container and structure shown in Figure 5, taken along the line IV—IV in Figure 5, into which is packed an assembly of a plurality of catalyst elements having another configuration.

Figure 5 is a schematic side view illustrating the structure shown in Figure 4 contain-

ing therein the catalyst containers in which is seen a plurality of catalyst layers (shown in Fig. 4) packed in each container.

Figures 6 and 7 are perspective views of the assembled structure for use in packing a plurality of catalyst elements within a catalyst container.

Figure 8 is a longitudinal-sectional view of the packing structure for the catalyst layers (taken along the line VIII—VIII in Fig. 6) disposed in multi-stages.

The catalyst element 1 shown in Fig. 1 is provided with corrugations 2 on the surface thereof and an appropriate number of perforations. While the catalyst element 1 shown in Fig. 4 is annular and is provided with a series of corrugations 2 on its outer surface.

Further, the catalyst elements shown in Figs. 6 and 7 are arranged in a flat-plate shape provided with a series of corrugations 2 on either one side or both sides thereof. And then these catalyst elements are fixed together in an appropriate assemblage, so as to be packed in a catalyst container 4, as shown in Figs. 5 and 8.

Furthermore, it should be noted that the end faces of the assemblage of a plurality of catalyst elements are to be protected with a wire gauze 5, as seen in Fig. 7.

#### Example 1.

A mixture obtained by 24 hours' dry blending of 7Kg of electrolytic manganese dioxide ( $MnO_2$ ) and 3Kg of red lead ( $Pb_3O_4$ ) both having a particle size of less than 200 mesh (i.e. 200 holes/sq. inch) by means of a ball-mill was introduced into the cavity of a die heated at  $400^\circ C$ . This charge, when its temperature rose to about  $400^\circ C$ , was subjected to 5 minutes' compacting under the pressure of 4 tonnes/cm<sup>2</sup>, whereby there was obtained a catalyst element as shown in Figures 1 and 2. The compressive breaking strength of this catalyst element was in the range of 200—300 Kg/cm<sup>2</sup>, 2—3 times as much as that of the pellet-shape catalysts available on the market.

Catalyst elements thus prepared were built into a cassette having a block-assemblage structure such as shown in Figure 3 and about 3 Kg of them were loaded into the catalyst container shown in Figure 5, into which waste gas at a temperature of about  $600^\circ C$ . from

the engine was exhausted. A follow-up survey of the composition of waste gas extending over about 400 hours in this case showed that the carbon monoxide (CO) concentration in the purified gas was kept below 1% and that the hydrocarbons (HC) concentration was kept below 100 ppm, indicating a conversion ratio of more than 90%, and there was also observed some converting effect with respect to nitrogen oxides. Besides, even after 400 hours' service, there was observed little change in the configuration of the catalyst elements, and no reduction in the efficiency of the engine.

#### Example 2.

For a catalyst element prepared by compacting a mixture of 5Kg of chemical manganese dioxide ( $MnO_2$ ) 3Kg of red lead ( $Pb_3O_4$ ) both having a particle size of less than 200 mesh, and 2Kg of electrolytic copper powder (Cu) having a particle size of 100 mesh, in the same way as in Example 1, the compressive breaking strength was in the range of 400—500 Kg/cm<sup>2</sup>, and a 300 hours' follow-up survey of the catalytic efficiency thereof showed that the conversion ratio for CO and HC was maintained around 90% and there was also observed some converting effect with respect to nitrogen oxide.

#### Example 3.

A mixture obtained by thoroughly mixing 1.5 Kg of electrolytic manganese dioxide ( $MnO_2$ ), 1.0 Kg of manganese sesquioxide ( $Mn_2O_3$ ), 7 Kg of red lead ( $Pb_3O_4$ ) all having a particle size of less than 200 mesh, and 3 Kg of iron powder (Fe) having a particle size of 100 mesh was processed in the same way as in Example 1, whereby corrugated catalyst elements were prepared. The compressive breaking strength of this catalyst element was in the range of 600—700 Kg/cm<sup>2</sup>, which is sufficient for use in an automobile. When the catalyst elements thus prepared were built into a block-assemblage structure as shown in Figure 7 and about 4 Kg of them were packed into a catalyst container and a follow-up survey of the catalytic efficiency thereof was conducted for about 400 hours in the same way as in Example 1, the conversion ratio as regards CO and HC was maintained around 70% as shown in the following Table 1.

TABLE 1

Purification data after 400 hours' service

condition of operation	concentrations in waste gas		concentrations in purified gas	
	CO (%)	HC (ppm)	CO (%)	HC (ppm)
idling	4.5	220	1.2	60
cruising (60 Km/hr.)	0.3	80	0.05	25

## Example 4.

5 A mixture consisting of 9.5 Kg of manganese sesquioxide ( $Mn_2O_3$ ), 500 g of bismuth sesquioxide ( $Bi_2O_3$ ), 500 g of lime and 500 g of lanthanum sesquioxide ( $La_2O_3$ ), all having the particle size of less than 200 mesh, was made into catalyst elements by the method of the invention and having the same configuration as that in Example 3. The thus prepared cata-

lyst elements were built into a block-assembly structure as shown in Figure 7 and about 4 Kg of them were packed into a catalyst cylinder. A follow-up survey of the catalytic efficiency of this structure conducted for about 300 hours in the same way as in Example 1 showed that the conversion ratio as regards CO and HC was maintained above 80% as shown in the following Table 2.

TABLE 2

Purification data after 300 hours' service

condition of operation	concentrations in waste gas		concentrations in purified gas	
	CO (%)	HC (ppm)	CO (%)	HC (ppm)
idling	4.6	230	0.8	45
cruising (60 Km/hr.)	0.4	90	0.08	15

## Example 5.

25 A mixture consisting of 5 Kg of electrolytic manganese dioxide ( $MnO_2$ ), 5 Kg of dibismuth pentoxide ( $Bi_2O_5$ ), 200 g of magnesia ( $MgO$ ), 300 g of ferric oxide ( $Fe_2O_3$ ), all having the particle size less than 200 mesh, and 1 Kg of iron powder (Fe) having the particle size of -100 mesh was made into catalyst elements by the method of the invention and having the same configuration as that in Example 3. The thus prepared cata-

lyst elements were built into a block-assembly structure as shown in Figure 6 and about 4 kg of them were packed into a catalyst container. A follow-up survey of the purification efficiency of this structure with respect to the waste gas conducted for about 400 hours in the same way as in Example 1 showed that the conversion ratio as regards CO and HC was maintained around 80% as shown in the following Table 3.

TABLE 3

Purification data after 400 hours' service

condition of operation	concentrations in waste gas		concentrations in purified gas	
	CO (%)	HC (ppm)	CO (%)	HC (ppm)
idling	4.8	250	0.9	50
cruising (60 Km/hr.)	0.5	90	0.1	15

## Example 6.

A variety of catalyst elements with different diameters, each having an annular shape with corrugations on the surface and made according to the process of the invention, were assembled by fitting into one after another, whereby a multi-layer packing structure such as shown in Figure 4 was prepared. A plurality of multi-layer packing structures thus prepared were packed into a catalyst container to form one multi-stage structure therein as shown in Figure 5, and the resultant catalyst container for use in purification of waste gas from automobiles proved to be much more efficient.

## Example 7.

A plurality of catalyst elements made according to the process of the invention and each comprising a rectangular sheet having one corrugated face were piled up into a multi-layer packing structure such as shown in Figure 6. A plurality of multi-layer packing structures thus prepared were stuffed into a catalyst container to form one multi-stage structure therein, and the resultant catalyst container for use in purification of waste gas from automobiles proved to have an improved purification efficiency.

## WHAT WE CLAIM IS:—

1. A method of moulding a catalyst element for use in purification of waste gas containing carbon monoxide, comprising compacting a catalyst powder composed mainly of a manganese oxide and either lead oxide or bismuth oxide to compacting at a temperature from 200—700° C., and at a pressure of 1—10 tonne/cm<sup>2</sup>.

2. A method according to claim 1 wherein the temperature is 300—500° C.

3. A method according to claim 1 or claim 2, in which the compacting is conducted after mixing at least one alkaline earth metal oxide, rare earth metal oxide (as herein defined), Al oxide, Si oxide, transition metal oxide, or transition metal, with said catalyst powder.

4. A method according to claim 1 or claim 2 in which the catalyst contains lead oxide and in which the compacting is conducted after mixing bismuth oxide with said catalyst powder.

5. A catalyst element whenever prepared according to the method of any preceding claim which is provided with wrinkles or corrugations on its surface and a number of holes penetrating therethrough.

6. A catalyst element according to claim 4, which is annular, or in sheet form or sector-shaped.

7. A catalyst assembly for use in the purification of waste gas containing CO, comprising an assemblage consisting of a plurality of catalyst elements of the kind claimed in either of claims 5 and 6 prepared according to claim 1, in a catalyst container.

8. A catalyst assembly for use in the purification of waste gas containing CO, comprising a plurality of catalyst elements prepared according to claim 1, having corrugated or wrinkled surfaces and have graduated diameters and which are concentrically fitted into a catalyst container.

9. A catalyst assembly for use in the purification of waste gas containing CO, comprising a stratiform catalyst structure composed of a plurality of catalyst elements, prepared according to claim 1, each element being sheet-shaped and having a corrugated or wrinkled surface, is fitted into a catalyst container.

10. A catalyst assembly for use in the purification of waste gas containing CO, comprising a catalyst layer composed of a plurality of catalyst elements prepared according to claim 1, each element presenting a sector-shaped section and having a corrugated or wrinkled surface and a plurality of through holes, which elements are so disposed as to form a circle in a catalyst container.

---

WITHERS & ROGERS,  
Chartered Patent Agents.  
148—150 Holborn,  
London, EC1N 2NT.  
Agents for the Applicants.

---

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1974.  
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.

FIG. 1

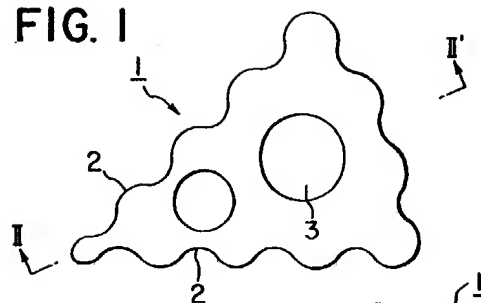


FIG. 2

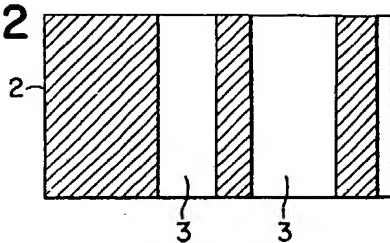


FIG. 3

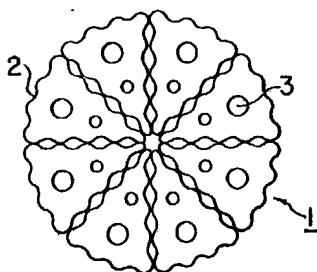


FIG. 4

